1,121,110

PATENT SPECIFICATION

NO DRAWINGS

1,121,110

Date of Application and filing Complete Specification: 3 Sept., 1965.

No. 37651/65.

Application made in United States of America (No. 398,744) on 23 Sept., 1964.

Complete Specification Published: 24 July, 1968.

Index at acceptance:—C2 C(2B47B1, 2B47G5, 2B47G7, 2B51B1, 2B51B3, 2B51G7, 2B52B1, 2B52B3, 2B53A2, 2B53K, P2L11A, P2L26A, P2L26E, P2L28, P2L29B, P7); A5 E(1C3B3, 1C4A2, 1C4A3, 1C4A4)

Int. Cl.:—C 07 c 131/00

COMPLETE SPECIFICATION

Carbamoyloximes

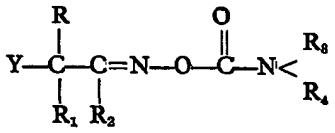
We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of LINWOOD KENNERLY PAYNE, Jr. and MATHIAS HERMAN JOSEPH WEIDEN), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel carbamoyloximes of α-electronegatively substituted carbonyl compounds. In the particular aspect, this invention is connected with novel α-electronegatively substituted carbamoylaldoximes and carbamoylketoximes.

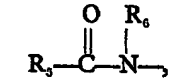
In addition to providing a novel class of carbamoyloximes this invention affords pesticidal, e.g., insecticidal, miticidal, and nematocidal compositions having activity comparable or superior to the most effective commercially used materials. The miticidal action of the carbamolyoximes encompassed herein is particularly important in that the mite pests are becoming increasingly troublesome and difficult to control inasmuch as they are often resistant to general insecticides and unaffected by specific insecticides used to control a particular crop pest.

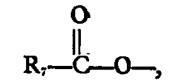
Accordingly, an object of this invention is to provide novel carbamoyloximes of α-electronegatively substituted carbonyl compounds. Another object is to provide novel α-electronegatively substituted carbamoylaldoximes and carbamoylketoximes. A further object is to provide novel α-electronegatively substituted, α-methyl, α-substituted N-methylcarbamoyloximes. Another object is to provide novel α-nitro, α-methyl, α-methyl N-methylcarbamoyloximes, and α-cyano, α-methyl, α-methyl N-methylcarbamoyloximes. A still further object is to provide novel carbamoyloximes which possess pesticidal properties such as insecticidal, nematocidal, and miticidal properties. Another object is to provide insecticidal, nematocidal, and miticidal compositions comprising novel carbamoyloximes as disclosed herein.

The novel carbamoyloximes of this invention can be represented by formula (I):

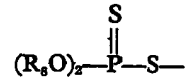
(I) 

wherein Y represents a nitro, cyano, thiocyanato,





or



group;

R and R_1 are each individually hydrogen or alkyl containing up to 4 alkyl carbon atoms with at least one of R and R_1 being alkyl at all times, preferably methyl; R_2, R_3, R_4, R_5, R_6 and R_7 are each individually hydrogen or alkyl containing up to 4 carbon atoms, preferably methyl; R_8 is alkyl, preferably methyl; R and R_1 or R_1 and R_2 can complete an aliphatic carbocyclic ring containing from 4 to 7 ring carbon atoms; when R and R_1 are both alkyl, one or more of the hydrogen atoms on one only of these two alkyl groups can be substituted; the aliphatic carbocyclic rings completed by $R+R_1$ or R_1+R_2 can be substituted.

Said substituents include cyano, nitro, methoxy, methylthio, halogen, trifluoromethyl, amido or thiocyanato. Additionally, when

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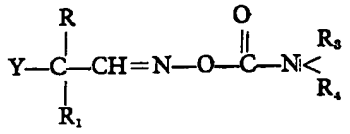
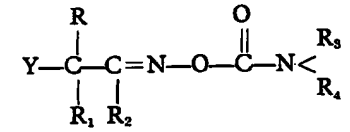
$R+R_1$ or R_1+R_2 complete on aliphatic carbocyclic ring, said ring can be substituted by alkyl containing up to 4 carbon atoms.

In a preferred aspect of this invention, the carbon atom attached to nitrogen through double bonds, is substituted with either hydrogen or methyl (R_2=H or CH_3—), and the carbon atom *alpha* thereto, carries at least one, and preferably two methyl groups (R and/or R_1=CH_3), while the carbamate nitrogen is substituted with two radicals individually selected from hydrogen and alkyl containing up to 4 alkyl carbon atoms, and preferably hydrogen and methyl (R_3 and/or R_4=H or CH_3), and preferably where the total number of carbon atoms in the R, R_1, R_2, R_3 and R_4 radicals together is not more than ten. It has been found that those carbamoyloximes having at least one methyl group on the carbon atom adjacent to the carbon atom attached to the nitrogen atom through double bonds, and not more than two such groups, are particularly good pesticides, as to be disclosed herein.

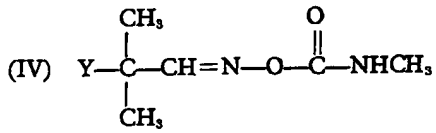
The novel carbamoyloximes of this invention can be further represented by formulae (II) and (III):

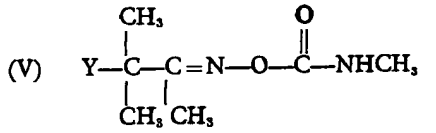
(II)


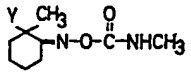
(III)


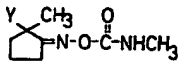
wherein Y, R, R_1, R_3, and R_4 are as hereinabove defined with reference to formula (I) and R_2 is alkyl containing up to 4 carbon atoms. The carbamoyloximes specifically represented by formula (II) can be referred to as the aldoximes of this invention and those carbamoyloximes specifically represented by formula (III) as the ketoximes of this invention. Both these oximes are contemplated as within the preview of this invention.

Particularly preferred carbamoyloximes of this invention can be represented by the aldoximes of formula (IV) and the ketoximes of formulae (V), (VI), and (VII):

(IV)


(V)


(VI)


(VII)


wherein Y is as defined hereinabove with reference to formula (I).

Representative carbamoyloximes encompassed within this invention include, among others, the carbamoyloximes, the N-methylcarbamoyloximes, the N,N - dimethylcarbamoyloximes, and the N-ethylcarbamoyloximes of the following aldehydes and ketones: 2-cyano-2-methylpropionaldehyde, 2-cyano-2-methyl-3-butanone, 2-cyano-2-methylcyclopentanone, 2-cyano-2-methylcyclohexanone, 2-cyano - 2 - methylbicyclo[2.2.1]heptan-3-one, 2-cyano-2,5-dimethylcyclohexanone, 2-cyano-5-isopropyl-2-methyl-cyclohexanone, 2-formyloxy-2-methylpropionaldehyde, 2-methyl - 2-acetoxypropionaldehyde, 2-methyl-2-(0,0'diethylthionophosphonothio) - propionaldehyde, 2-thiocyanato-2 - methylpropionaldehyde, 2-formamido-2-methylpropionaldehyde, 2-acetamido-2 - methylpropionaldehyde, 2 - (N'-methylformamido)-2 - methylpropionaldehyde, 2-formamido-2-methyl-3-butanone, 2 - acetamido-2-methyl-3-butanone, 2-methyl-2-nitropropionaldehyde, 2-methyl-2-nitro-3-butanone, 2-methyl-2-nitrocyclobutanone, 2 - methyl-2-nitrocyclopentanone, 2-methyl-2-nitrocyclohexanone, 2-methyl-2-nitrocycloheptanone, 2-methyl-2-nitrobicyclo[2.2.1]heptan-3-one, 2-methyl-2-nitro(4 or 5)-cyanocyclohexanone, 2-ethyl-2-nitrocyclopentanone, 2-ethyl-2-nitrocyclohexanone, 3-ethyl-3-nitro-2-pentanone, methyl 1-nitrocyclopentyl ketone, 2-nitro-2, 5-dimethylcyclohexanone, 2-nitro-5-isopropyl-2-methyl-cyclohexanone, 2-methyl-2-cyanocyclobutanone, 2-methyl-2-cyano-cycloheptanone, 2-methyl-2-cyano-(4 or 5)-nitrocyclohexanone, 2-ethyl-2-cyanocyclopentanone, 2-ethyl - 2-cyanocyclohexanone, 2-ethyl-2-cyano-3-pentanone and methyl 1-cyanocyclopentyl ketone.

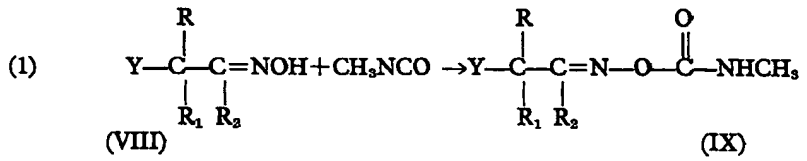
The carbamoyloximes of this invention may be prepared, for example, as follows:

A. *Oxime* — A nitrosochloride dimer is reacted with a slight excess of sodium nitrite (or sodium cyanide) (1.1 mole of sodium nitrite (or cyanide) per equivalent of chlorine) by adding the dimer to a suspension of sodium nitrite (or cyanide) in dimethylsulfoxide. The addition is conducted with rapid agitation and maintaining a reaction temperature of 20—65°C. for sufficient time to insure reaction (usually 2—3 hours although up to 60 hours

may be required). After filtering the reaction mixture to remove sodium chloride, the solvent is removed by stripping under reduced pressure. The residue product is dissolved in an inert water-insoluble solvent such as ether, the ether solution is washed with water to remove any remaining dimethylsulfoxide and then the ether is removed by stripping under reduced pressure. The residue oxime may be purified by recrystallization. The introsochloride dimers used to prepare the oxime precursors are prepared by the addition of nitrosyl chloride to a suitable olefin by well-known procedures, for example, as taught in *J. Gen. Chem.*, (U.S.S.R.), *22*, 2175 (1952).

B. *N-Methyl Carbamate* — To a solution of the oxime in an inert solvent, if desired, such as diethyl ether or acetone, is added an equimolar quantity of methyl isocyanate. The reaction is conducted, at the boiling point of the reaction mixture and can be carried out in the presence of a catalytic amount of well-known catalysts such as dibutyltin diacetate or di-2-ethylhexanoate, pyridine, triethylamine, or 1,4-diazabicyclo[2.2.2]octane. After sufficient time, usually about 3—6 hours, for the reaction to be completed, the solvent, if employed, is removed by stripping under reduced pressure, and the crude product may be purified by recrystallization. This procedure works well with or without a catalyst and additional solvent is not required as methyl isocyanate itself can serve as solvent.

The synthetic route for preparing the carbamoyloximes of this invention from the corresponding oximes involving the addition of methyl isocyanate can be illustrated as follows:



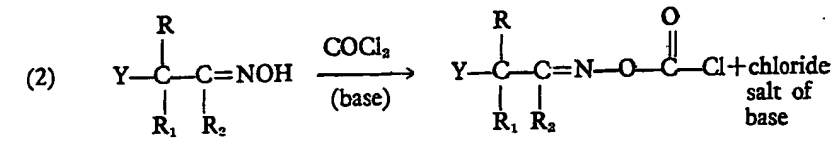
(1) $Y-\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}-\underset{\underset{R_2}{|}}{C}=NOH + CH_3NCO \rightarrow Y-\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}-\underset{\underset{R_2}{|}}{C}=N-O-\overset{\overset{O}{\|}}{C}-NHCH_3$

(VIII) (IX)

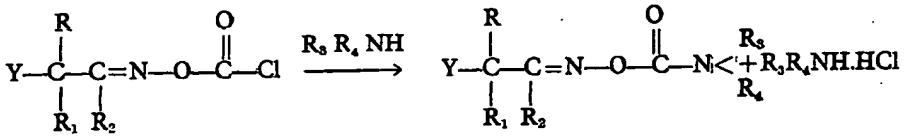
wherein R, R_1 and R_2 are as hereinabove defined with reference to formula (I).

Reaction (1) can be carried out by contacting the oxime (VIII) with methyl isocyanate in an inert organic solvent, and preferably in the presence of a tertiary amine or organotin catalyst. The reaction may be effected at temperatures ranging from 10°C. to 130°C., and is preferably carried out between room temperature and 80°C. Generally, temperatures in excess of 130°C. are to be avoided in view of the temperature sensitivity of the product carbamoyloxime. The operating pressure may range from 1 atmosphere to 10 atmospheres, absolute preferably from 2 to 3 atmospheres absolute, and is dependent upon the concentration and vapor pressure of the volatile isocyanate at the reaction temperature. The inert organic solvents that can be employed in the reaction, when additional solvent is desired, are those inert to isocyanates in general, i.e., those free of radicals such as hydroxy or amino radicals. Illustrative solvents are aliphatic and aromatic hydrocarbons, such as hexane, heptane, octane, benzene and toluene, and ethers such as diethyl ether and diisopropyl ether. Other solvents which can be employed include ketones such as methyl ethyl ketone and acetone; nitriles such as acetonitrile; and halocarbons such as chloroform and methylene chloride. The ketones and acetonitrile are the solvents of preference. The reaction is preferably carried out in the presence of a tertiary amine or organotin catalyst. The term "organotin catalyst" as used herein is meant to refer to such compounds as dibutyltin diacetate, dibutyltin dichloride, dibutyltin dimethoxide, dibutyltin dilaurate, dibutyltin maleate, dibutyltin di-2-ethylhexenoate, stannous octanoate and stannous oleate. Generally, amounts of said catalyst from 0.1 to 1.0 weight per cent of the starting material comprised of methyl isocyanate and the oxime are sufficient. The mol ratio of methyl isocyanate to oxime is preferably an equiomolar amount or excess of methyl isocyanate so as to insure that the oxime is completely reacted. The reaction time may vary from 5 minutes to 7 days, but normally, when operating in the preferred temperature range, reaction times of from one-half hour to five hours are sufficient for complete reaction. The carbamoyloxime product formed, either as a solid or oily liquid, can be recovered from the reaction mixture by means known to the art, e.g., by vacuum distillation to drive off solvent and excess isocyanate.

The carbamoyloximes of this invention also may be prepared by the reaction of the corresponding oxime with phosgene to form the chloroformate which, in turn, is reacted with ammonia or amines, for example, ammonia to give the carbamoyloxime or methylamine to give the N-methylcarbamoyloxime or dimethylamine to give the N,N-dimethylcarbamoyloxime. The synthesis is illustrated by the following general reaction scheme:

(2) 

(VIII) (X)



(X) (XI)

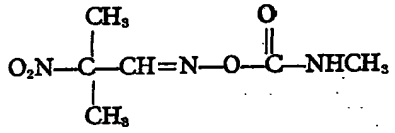
wherein Y, R, R_1 and R_2 are as hereinabove defined with reference to formula (I).

In step (2), a solution of the phosgene in, e.g., toluene or diethyl ether is conveniently added dropwise to a solution of the oxime compound (VIII) in toluene or diethyl ether in the presence of an HCl acceptor such as dimethyl aniline. (The dimethyl aniline is usually in the phosgene solution). The reaction can be carried out at from −30°C. to 40°C. but will generally be found to proceed most advantageously between 0°C. and room temperature. Below 0°C. the reaction is somewhat sluggish and if the temperature is allowed to rise substantially above 40°C., considerable quantities of nitrile from the dehydration of the aldoxime compound will appear in the reaction mixture. The reaction is slightly exothermic so that some external cooling is usually necessary to maintain the temperature within the desired range. The reaction mixture can be washed with water to remove the amine hydrochloride and the organic layer containing the chloroformate can be used for further reactions. The addition of amine step (3) above, is carried out in the presence of solvents for the amine, such as water, dioxane, toluene, or chloroform, at temperatures between −40°C. and 80°C., and preferably below 40°C. inasmuch as the reaction precedes smoothly even at low temperatures and is so rapid above 40°C. that loss of low boiling amines may occur and some decomposition may take place.

The following Examples are illustrative:

EXAMPLE I.

2-Methyl-2-Nitropropionaldehyde N-Methylcarbamoyloxime.



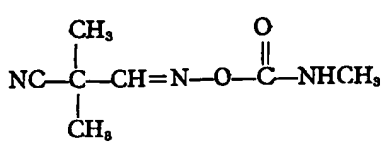
2-Nitro-2-methylpropionaldehyde oxime (9 gms.: 0.076 mole) was reacted with methyl isocyanate (5 gms.: 0.088 mole) in 50 ml. of anhydrous diethyl ether using dibutyltin diacetate as a catalyst to give 2-nitro-2-methylpropionaldehyde N-methyl carbamoyloxime. After recrystallization from isopropanol there was obtained 8 gms. of 2-nitro-2-methylpropionaldehyde N-methylcarbamoyloxime as a white solid, m.p. 85—86°C. The infrared spectrum showed carbamate C=O at 5.8μ, NH at 3.0μ, NO_2 at 6.35μ and 7.45μ, carbamate C—O at 8.0μ, and C=N—O at 10.54μ.

Anal.

Calc'd. for $C_6H_{11}N_3O_4$: C, 38.2; H, 5.8; N, 22.2
Found: C, 38.3; H, 6.1; N, 22.5

EXAMPLE II.

2-Cyano-2-Methylpropionaldehyde N-Methylcarbamoyloxime.



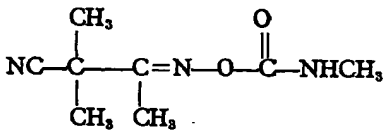
2-Cyano-2-methylpropionaldehyde oxime (4 gms. 0.035 mole) was heated with methylisocyanate (2.28 gms.; 0.04 mole) in anhydrous diethyl ether for six hours with dibutyltin diacetate catalyst to give 2-cyano-2-methylpropionaldehyde N - methylcarbamoyloxime. After recrystallizing from diethyl ether there was obtained 5 gms. of 2-cyano-2-methylpropionaldehyde N-methylcarbamoyloxime as a

white solid, m.p. 80—82°C. The infrared spectrum indicated carbamate NH at 2.9μ and 6.61μ, C≡N at 4.42μ, carbamate C=O at 5.74μ and C=N—O— at 10.25 and 10.50μ.

Anal.
Calc'd. for $C_7H_{11}N_3O_2$: C, 49.7; H, 6.5; N, 24.8
Found: C, 49.9; H, 6.4; N, 24.6

EXAMPLE III.

2-Cyano-2-Methyl-3-Butanone N-Methylcarbamoyloxime.

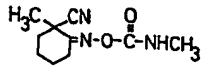


2-Cyano-2-methyl-3-butanone oxime (13 gms.; 0.1 mole) was dissolved in 100 ml. of diethyl ether and treated with methyl isocyanate (6.2 gms.; 0.11 mole) and a catalytic amount of dibutyltin diacetate. After standing for 20 hours the resulting precipitate was collected by filtration, washed thoroughly with ethyl ether, and dried. There was obtained 16 gms. (87.5% yield) of 2-cyano-2-methyl-3-butanone N-methylcarbamoyloxime; m.p. 70—71°C.

Anal.
Calc'd. for $C_8H_{13}N_3O_2$: C, 52.4; H, 7.2; N, 22.9
Found: C, 52.5; H, 7.5; N, 23.2
Infrared: N—H at 2.93μ and 6.60μ; CH_3 at 3.34μ; C≡N at 4.42μ; C=O at 5.90μ; C=N at 6.08μ; C—O at 8.10μ and C=N—O at 10.5μ

EXAMPLE IV.

2-Cyano-2-Methylcyclohexanone N-Methylcarbamoyloxime.

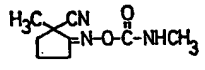


2-Cyano-2-methylcyclohexanone oxime (10 gms.; 0.066 mole) was dissolved in 150 ml. of anhydrous diethyl ether and treated with methyl isocyanate (4.1 gms.; 0.072 mole) and one drop of dibutyltin diacetate. The solution was stirred at ambient temperature for 20 hours. The ether solution was washed well with water, dried, filtered, and stripped to a clear viscous residue. The 2-cyano-2-methylcyclohexanone N - methylcarbamoyloxime weighed 13 gms., (94% yield).

Anal.
Calc'd. for $C_{10}H_{15}N_3O_2$: C, 57.4; H, 7.2; N, 20.0
Found: C, 57.1; H, 7.4; N, 19.7
Infrared: N—H at 2.95μ and 6.65μ; C≡N at 4.49μ; C=O at 5.8μ; C=N at 6.1μ; C—O at 9.15μ, and C=N—O at 10.6μ.

EXAMPLE V.

2-Cyano-2-Methylcyclopentanone N-Methylcarbamoyloxime.

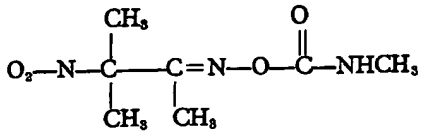


2-Cyano-2-methylcyclopentanone oxime was allowed to react with methyl isocyanate in diethyl ether solution along with a catalytic amount of dibutyltin diacetate. The solid which precipitated was collected by filtration and washed well with diisopropyl ether to give 7 gms. (90% yield) of 2-cyano-2-methylcyclopentanone N - methylcarbamoyloxime; m.p. 70—72°C.

Anal.
Calc'd. for $C_9H_{13}N_3O_2$: C, 55.4; H, 6.7; N, 21.5.
Found: C, 55.6; H, 7.0; N, 21.2.
Infrared: N—H at 3.0μ and 6.63μ; CH_3/CH_2 at 3.35μ, 3.42μ, and 3.5μ; C≡N at 4.5μ; C=O at 5.85μ; C=N at 6.03μ; C—O at 8.1μ, and C=N—O at 10.5μ.

EXAMPLE VI.

2-Methyl-2-Nitro-3-Butanone N - Methylcarbamoyloxime.



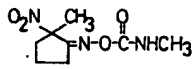
2-Methyl-2-nitro-3-butanone oxime (8 gms.; .055 mole) was reacted with methyl isocyanate (3.5 gms.; .06 mole) in diethyl ether solvent at 30—35°C. for six hours producing 2-methyl-2-nitro-3-butanone N - methylcarbamoyloxime in 89% yield. Dibutyltin diacetate was employed as a catalyst. The 2-methyl-2-nitro-3-butanone N - methylcarbamoyloxime melts sharply at 116—117°C. when recrystallized from isopropanol.

Anal.

Calc'd. for $C_7H_{13}N_3O_4$: C, 41.4; H, 6.4; N, 20.7
Found: C, 41.6; H, 6.7; N, 19.7

EXAMPLE VII.

2-Methyl-2-Nitrocyclopentanone N-Methylcarbamoyloxime.



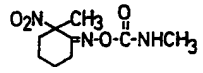
2-Methyl-2-nitrocyclopentanone oxime 7.9 gms.; .05 mole), was dissolved in 150 ml. anhydrous diethyl ether, and allowed to react one day at 30°C. with methyl isocyanate (3.1 gms.; .055 mole) in the presence of one drop of dibutyltin diacetate. The residue obtained after evaporation of the solvent was recrystallized from diisopropyl ether to give 8 gms. of 2-methyl-2-nitrocyclopentanone N - methylcarbamoyloxime as a white solid; m.p. 92—93°C.

Anal.

Calc'd. for $C_8H_{13}N_3O_4$: C, 44.6; H, 6.1; N, 19.5
Found: C, 45.1; H, 6.2; N, 19.3.
Infrared analysis indicates NH at 3.0μ and 6.65μ, C=O at 5.85μ, C—O at 8.09μ, C=N at 6.02μ, NO_2 at 6.45μ and 7.35μ and C=N—O at 10.5μ.

EXAMPLE VIII.

2-Methyl-2-Nitrocyclohexanone N-Methylcarbamoyloxime.



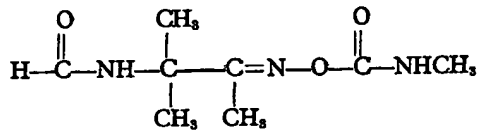
2-Methyl-2-nitrocyclohexanone oxime was reacted with methyl isocyanate using the procedure described for the cyclopentyl analog in Example VII, to give 2-methyl-2-nitrocyclohexanone N-methylcarbamoyloxime in 96% yield. The product was taken as a viscous oil.

Anal.

Calc'd. for $C_9H_{15}N_3O_4$: C, 47.1; H, 6.6; N, 18.3
Found: C, 47.4; H, 6.8; N, 18.2
Infrared: NH at 2.98μ and 6.63μ; C=O at 5.8μ; C=N at 6.1μ; NO_2 at 6.45μ and and 7.45μ, at 8.13μ and C=N—O at 10.55μ.

EXAMPLE IX.

2-Formamido-2 - Methyl-3 - Butanone N- Methylcarbamoyloxime.

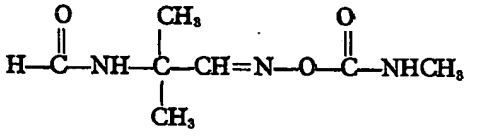


2-Formamido-2-methyl-3-butanone oxime (8 gms.; 0.056 mole) was dissolved in 100 ml. of anhydrous diethyl ether and treated with methyl isocyanate (3.5 gms.; 0.062 mole) and two drops of dibutyltin diacetate. After standing for sixteen hours the reaction mixture was filtered and the crystals washed with diethyl ether. 6 Grams (53 per cent yield) of 2-formamido-2 - methyl - 3-butanone N-methyl-carbamoyloxime was obtained m.p. 118—120°C.

Anal.
Calc'd. for $C_8H_{15}N_3O_3$: C, 47.7; H, 7.5; N, 20.9
Found: C, 47.4; H, 7.3; N, 20.7
Infrared: N—H at 2.94μ, 3.05μ, 6.55μ and 6.65μ; carbamate C=O at 5.80μ; amide C=O at 5.97μ; carbamate C—O at 8.03 and C=N—O at 10.52μ

EXAMPLE X.

2-Formamido-2-Methylpropionaldehyde N-methylcarbamoyloxime.

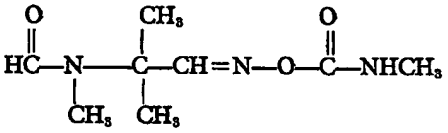


2-Formamido - 2 - methylpropionaldehyde oxime was obtained by allowing 2-amino-2-methylpropionaldehyde oxime (12.6 g.; 0.124 mole) to react for three hours at 35°C. with vinyl formate (10 g.; 0.14 mole) in 200 ml. of anhydrous acetone. The solvent was evaporated under reduced pressure. The residual 2-formamido-2-methylpropionaldehyde oxime was dissolved in 200 ml. of chloroform and treated with methylisocyanate (7.6 g.; 0.134 mole) and 1 drop of dibutyltin diacetate. After two hours at 35°C. the solvent was evaporated under reduced pressure and the residue was stirred with 150 ml. of ethyl acetate. The precipitate was collected by filtration washed with petroleum ether and dried. 2-Formamido-2-methylpropionaldehyde N-methylcarbamoyloxime, m.p. 113—115°C., was obtained in 52 per cent yield.

Anal.
Calc'd. for $C_7H_{13}N_3O_3$: C, 44.9; H, 7.0; N, 22.7
Found: C, 44.6; H, 7.2; N, 22.4

EXAMPLE XI.

2 - (N'-Methylformamido)-2-Methylpropionaldehyde N-Methylcarbamoyloxime.

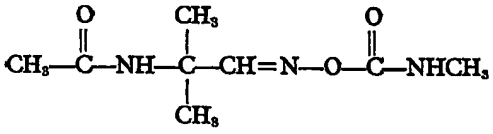


2-(N-methylformamido)-2 - methylpropionaldehyde oxime (4 gms.; 0.027 mole) was dissolved in 200 ml. of anhydrous acetone and heated at 40°C. for eight hours with methyl isocyanate (1.7 gms.; 0.3 mole). The solvent was stripped in vacuo and the residue heated to 50°/3mm. 2-(N'-Methylformamido)-2-methylpropionaldehyde N-methylcarbamoyloxime was obtained as a viscous oil weighing 5 gms. (92 per cent yield).

Anal.
Calc'd. for $C_8H_{15}N_3O_3$: C, 47.8; H, 7.5; N, 20.9
Found: C, 47.6; H, 8.0; N, 20.4
Infrared: Carbamate N—H, 3.0μ and 6.6μ; carbamate C=O, 5.82μ; carbamate C—O, 8.05μ; C=N—O, 10.55μ; amide C=O, 6.05μ. Weak C≡N impurity noted at 4.48μ.

EXAMPLE XII.

2-Acetamido - 2 - Methylpropionaldehyde N- Methylcarbamoyloxime.

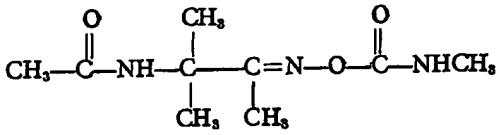


2-Acetamido - 2 - methylpropionaldehyde oxime was treated with methyl isocyanate in chloroform solution to produce 2-acetamido-2-methylpropionaldehyde N-methylcarbamoyloxime in 46 per cent yield; m.p. 143—145°C (ethyl acetate).

Anal.
Calc'd. for $C_8H_{15}N_3O_3$: C, 47.7; H, 7.5; N, 20.9
Found: C, 48.1; H, 7.8; N, 21.1
Infrared: Carbamate C=O at 5.78μ; amide C=O at 6.08μ; carbamate C—O at 7.93μ and C=N—O at 10.7μ.

EXAMPLE XIII.

2-Acetamido-2-Methyl-3-Butanone N-Methyl-carbamoyloxime.



2-Acetamido-2-methyl-3-butanone oxime (4 gms.; 0.025 mole) was dissolved in 70 ml. of dimethylformamide and treated with methyl isocyanate (1.7 gms.; 0.03 mole) and two drops of dibutyltin diacetate for sixty hours at room temperature. The solvent was evaporated under reduced pressure and the residue treated with 100 ml. of diethyl ether. The resulting solid was collected by filtration, washed with diethyl ether and dried. There was obtained 5 gms. (93 per cent yield) of 2-acetamido-2-methyl-3-butanone N - methylcarbamoyloxime, m.p. 100—103°C.

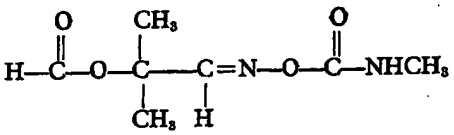
Anal.

Calc'd. for $C_8H_{17}N_3O_3$: C, 50.2; H, 8.0
Found: C, 48.6; H, 8.4

Infrared: N—H at 2.95μ, 3.04μ, 6.4μ, and 6.65μ; carbamate C=O at 5.8μ; amide C=O at 6.08μ; carbamate C—O at 8.08μ and C=N at 10.54μ.

EXAMPLE XIV.

2-Formyloxy - 2-methylpropionaldehyde N- methylcarbamoyloxime.



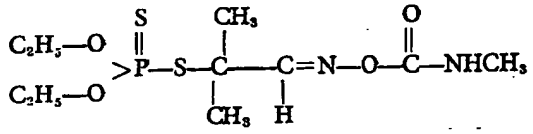
2-Formyloxy - 2 - methylpropionaldehyde oxime (11 g.; 0.084 mole) was dissolved in 150 ml. of anhydrous diethyl ether and treated with methyl isocyanate (5.3g.; 0.092 mole) and two drops of dibutyltin diacetate. After standing at ambient temperature for sixteen hours the ether solution was washed thoroughly with water, dried over magnesium sulfate, filtered, and the solvent evaporated. There was obtained 14 g. of 2-formoxy-2-methylpropionaldehyde N-methylcarbamoyloxime as a colorless oil.

Anal.

Calcd. for $C_7H_{12}N_2O_4$: C, 44.7; H, 6.4; N, 14.9
C, 44.7; H, 6.7; N, 14.3

EXAMPLE XV.

2-Methyl-2 - (O,O'-Diethylthionophosphono- thio)propionaldehyde N-Methylcarbamoyloxime.



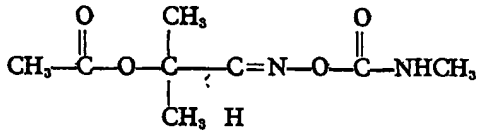
2-Methyl - 2 - (O',O - diethylthionophosphonothio)propionaldehyde N-methylcarbamoylamine was obtained as a residual oil by allowing 2-methyl-2 - (O,O' - diethylthionophosphonothio)propionaldehyde oxime to react with methylisocyanate as in Example XIV. The infrared spectrum was consistent with the proposed structure. The 2-methyl-2-(O,O'-diethylthionophosphonothio) propionaldehyde oxime precursor was obtained by reacting O,O'-diethyldithiophosphoric acid and sodium hydroxide dissolved in ethanol with 2-chloro-2-methyl-1-nitrosopropane dimer.

Anal.

Calc'd. for $C_{10}H_{21}S_2O_4N_2P$: C, 36.5; H, 6.4; N, 8.5
Found: C, 36.1; H, 6.5; N, 8.4

EXAMPLE XVI.

2-Methyl - 2 - Acetoxypropionaldehyde N- Methylcarbamoyloxime.



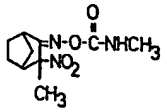
2-Methyl-2 - acetoxypropionaldehyde N-methylcarbamoyloxime was prepared as a colorless oil by reacting 2-methyl-2-acetoxypropionaldehydeoxime dissolved in diisopropyl ether with methyl isocyanate in the presence of dibutyltin diacetate. The precursor 2-methyl-2-acetoxypropionaldehyde oximes was prepared from anhydrous potassium acetate and 2-chloro-2-methyl-1-nitrosopropane dimer according to *J. Gen. Chem.*, (USSR), *22*, 2175 (1952).

Anal.

Calc'd. for $C_8H_{14}N_2O_4$: C, 47.5; H, 7.0; N, 13.8
Found: C, 47.6; H, 7.2; N, 14.1

EXAMPLE XVII.

2-Methyl-2 - Nitrobicyclo[2.2.1]heptan - 3-one N-Methylcarbamoyloxime.



2-Methyl-2 - nitrobicyclo[2.2.1]heptan - 3-one N-methylcarbamoyloxime was prepared in 65 per cent yield by reacting 2-methyl-2-nitrobicyclo[2.2.1]heptan-3-one oxime with methyl isocyanate. The resultant 2-methyl-2-nitrobicyclo[2.2.1]heptan-3-one N - methylcarbamoyloxime melted at 129—131°C when recrystallized from ethanol-water (50.50).

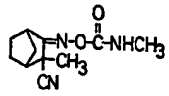
Anal.

Calc'd. for $C_{10}H_{15}N_3O_4$: C, 49.8; H, 6.2; N, 17.4
Found: C, 49.7; H, 6.4; N, 17.2.

Infrared: Carbamate NH at 2.89μ, 2.95μ and 6.65μ; carbamate C=O at 5.75μ; C=N at 5.97μ; NO_2 at 6.47μ and 7.42μ; carbamateC—O at 8.15μ and C=N—O at 10.53μ and 10.63μ.

EXAMPLE XVIII.

2-Cyano-2 - Methylbicyclo[2.2.1]heptan - 3- one N-Methylcarbamoyloxime.



In a manner similar to that of Example XVII, 2-cyano-2-methylbicyclo[2.2.1]heptan-3-one N-methylcarbamoyloxime was prepared, m.p. 115—117°C.

Anal.

Calc'd. for $C_{11}H_{15}N_3O_2$: C, 59.7; H, 6.8; N, 19.0.
Found: C, 59.9; H, 6.9; N, 18.7.

Other carbamoyloximes encompassed within this invention are found in Table I.

TABLE I
N-Methyl Carbamoyloximes

Example	Compound Name	m.p., °C.	Elemental Analysis C Calc.	C Found	H Calc.	H Found	N Calc.	N Found
XIX	2-Methyl-2-nitrocycloheptanone N-methylcarbamoyloxime	64	49.4	49.4	7.0	7.3	17.3	16.7
XX	5-Cyano-2-methyl-2-nitrocyclo-hexanone N-methylcarbamoyloxime	184—185	47.3	48.1	5.5	6.1		
XXI	Methyl 1-nitrocyclopentyl ketone N-methylcarbamoyloxime	92	47.2	47.5	6.6	6.9	18.3	18.1
XXII	2-Ethyl-2-nitrocyclopentanone N-methylcarbamoyloxime	99—101	47.2	46.9	6.6	6.6	18.3	18.0
XXIII	2-Ethyl-2-nitrocyclohexanone N-methylcarbamoyloxime	49.4	49.2	49.2	7.0	7.2	17.3	17.3
XXIV	3-Ethyl-3-nitro-2-pentanone N-methylcarbamoyloxime	Residue					18.3	17.9
XXV	2-Methyl-2-nitrocyclobutanone N-methylcarbamoyloxime	Residue	41.8	42.1	5.5	6.0	20.9	19.5
XXVI	2-Cyano-2,5-dimethylcyclohexanone N-methylcarbamoyloxime	124—128	59.2	59.0	7.7	7.7	18.8	18.7
XXVII	2-Cyano-5-isopropyl-2-methyl-cyclohexanone N-methylcarbamoyloxime	123—130	62.1	61.9	8.4	8.4	16.7	16.2
XXVIII	2-Methyl-2-nitro-5-isopropyl-cyclohexanone N-methylcarbamoyloxime	95—105	53.0	53.3	7.8	7.9	15.5	15.3
XXIX	2-Cyano-5-isopropenyl-2-methyl-cyclohexane N-methylcarbamoyloxime	123—125	62.6	62.9	7.7	7.9	16.9	16.5

The carbamoyloximes of this invention show particular promise as pesticides. They are particularly useful in agricultural applications to combat undesirable organisms which adversely effect plant life. The carbamoyloximes disclosed herein have been shown to be particularly active as insecticides, nematocides and miticides.

The carbamoyloxime, 2-methyl-2-nitropropionaldehyde N - methylcarbamoyloxime, has been shown to be an extremely active miticide and an excellent insecticide with broad activity. 2-Cyano-2-methylpropionaldehyde N-methylcarbamoyloxime has been shown to be a powerful pesticide with broad activity as it shows excellent control, for insects such as the bean aphid, the Mexican bean beetle and the housefly. Both the 2-methyl-2-nitro- and 2-cyano-2-methylpropionaldehyde N-methylcarbamoyloximes have been shown to control (LD_{50}) the southern army worm at dosages below 100 parts per million. The carbamoyloximes disclosed herein have shown significant insecticidalmiticidal properties, for example 2-cyano-2-methylcyclopentanone N - methylcarbamoyloxime shows good activity against the two-spotted mite and housefly; 2-methyl-2-nitrobutan-3-one N-methylcarbamoyloxime shows good activity against the two-spotted mite, Mexican bean beetle and housefly; 2-methyl-2-nitrocyclohexanone N-methylcarbamoyloxime shows promise against the Mexican bean beetle and bean aphid, 2-methyl-2-nitrocyclopentanone N-methylcarbamoyloxime is active against the two-spotted mite, bean aphid, Mexican bean beetle and housefly; and 2-cyano-2-methylcyclohexanone N-methylcarbamoyloxime is active against the bean aphid and Mexican bean beetle.

2-Formamido-2 - methylbutan-3-one N-methylcarbamoyloxime has exhibited for example, significant toxic properties to the two-spotted mite. The carbamoyloxime, 2-formamido-2-methylpropionaldehyde N-methylcarbamoyloxime has been shown to be highly toxic to the two-spotted mite, the bean aphid, the common housefly, and the root-knot nematode. 2-Acetamido-2-methylpropionaldehyde N-methylcarbamoyloxime and 2-(N'-methylformamide)-2 - methylpropionaldehyde N-methylcarbamoyloxime show a similar spectrum of activity to pests.

Table II infra, illustrates carbamoyloximes of this invention and their pesticidal activity.

TABLE II
Biological Activity of N-Methyl Carbamoyloximes[1]

Example	Compound Name	LD_{50} (ppm)					ED_3(lbs/Acre)
		BA	M	AW	MBB	HF	NEMA
1	2-Methyl-2-nitropropionaldehyde N-methylcarbamoyloxime	6	10[10]	55	80	3	15
2	2-Cyano-2-methylpropionaldehyde N-methylcarbamoyloxime	10	40	55	65	3	>75
3	2-Cyano-2-methyl-3-butanone N-methylcarbamoyloxime	>100	120	500	70	20	19
4	2-Cyano-2-methylcyclohexanone N-methylcarbamoyloxinme	20	100	1000	15	50	50
5	2-Cyano-2-methylcyclopentanone N-methylcarbamoyloxime	80	20	350	50	22	>19
6	2-Methyl-2-nitro-3-butanone N-methylcarbamoyloxime	60	25[10]	600	25	28	19
7	2-Methyl-2-nitrocyclopentanone N-methylcarbamoyloxime	12	12[8] (200)	1200	12	30	*
8	2-Methyl-2-nitrocyclohexanone N-methylcarbamoyloxime	15	60	>1000	8	120	50
9	2-Formamido-2-methyl-3-butanone N-methylcarbamoyloxime	>100	30	1000	>100	120	>75
10	2-Formamido-2-methylpropionaldehyde N-methylcarbamoyloxime	6	15	330	150	2	4.8

TABLE II (Continued)

Biological Activity of N-Methyl Carbamoyloximes

Example	Compound Name	LD_{50} (ppm)					ED_8(lbs/Acre)
		BA	M	AW	MBB	HF	NEMA
11	2-(N'-methylformido)-2-methyl propionaldehyde N-methylcarbamoyloxime	12	16	>1000	100	10	19
12	2-Acetamido-2-methylpropionaldehyde N-methylcarbamoyloxime	12	17	>1000	>100	4	50
13	2-Acetamido-2-methyl-3-butanone N-methylcarbamoyloxime	100	400	>1000	>100	800	>75
14	2-Formyloxy-2-methylpropionaldehyde N-methylcarbamoyloxime	20	1000	325	>100	26	>75
15	2-Methyl-2-(O,O'-diethylthionophosphonothio)-propionaldehyde N-methylcarbamoyloxime	>100	150	>1000	>100	75	>75
16	2-Methyl-2-acetoxypropionaldehyde N-methylcarbamoyloxime	15	150[40]	500	>100	40	>75
17	2-Methyl-2-nitrobicyclo[2.2.1]-heptan-3-one N-methylcarbamoyloxime	12	15[160]	>1000	75	120	>75
18	2-Cyano-2-methylbicyclo[2.2.1]-heptan-3-one N-methylcarbamoyloxime	100	130	>1000	>100	170	>75
19	2-Methyl-2-nitrocyclopheptanone N-methylcarbamoyloxime	>100	125	>1000	>100	>1000	>75

TABLE II (Continued)
Biological Activity of N-Methyl Carbamoyloximes

Example	Compounded Name	LD_{50} (ppm) BA	M	AW	MBB	HF	ED_3(lbs/Acre) NEMA
20	(5 or 4)-Cyano-2-methyl-2-nitro-cycloheanone N-methylcarbamoyloxime	>100	15	1000	100	40	60
21	Methyl-1-nitrocyclopentyl ketone N-methylcarbamoyloxime	>100	125	>1000	>100	1000	>75
22	2-Ethyl-2-nitrocyclopentanone N-methylcarbamoyloxime	>100	500	>1000	30	200	*
23	2-Ethyl-2-nitrocyclohexanone N-methylcarbamoyloxime	>100	1000	>1000	30	1200	*
24	3-Ethyl-3-nitro-2-pentanone N-methylcarbamoyloxime	>100	1000	>1000	100	125	>75
25	2-Methyl-2-nitrocyclobutanone N-methylcarbamoyloxime	10	500	500	>100	10	5
26	2-Cyano-2,5-dimethylcyclohexanone N-methylcarbamoyloxime	60	>1000	>1000	50	125	>75
27	2-Cyano-5-isopropyl-2-methyl-cyclohexanone N-methylcarbamoyloxime	>100	1000	>1000	50	>1000	>75

[1] BA = Bean Aphid
M = Two-Spotted Mite
AW = Southern Armyworm
MBB = Mexican Bean Beetle
HF = House Fly
NEMA = Root-Knot Nematode

ED_3 = a given concentration of N-methylcarbamoyloxime which will elicit a rating of "3" (light galling) on a scale of "1 to 5". As used, herein, the term ED_3 is for all practical purposes synonymous with the term LD_{50}; but in pounds/acre.
[ ] = systemic activity
( ) = ovacidal activity
* = phytotoxic to host at 19 pounds/acre

The carbamoyloximes of this invention have been tested for activity against the following representative pests: bean aphid, armyworm, Mexican bean beetle, housefly, two-spotted mite, and root-knot nematode.

The tests employed and shown in the Tables herein are as follows:

Aphid Foliage Spray Test

Adults and nymphal stages of the bean aphid (*Aphis fabae Scop.*), reared on potted dwarf nasturtium plants at 65—70°F. and 50—70 per cent relative humidity, consituted the test insects. For testing purposes, the number of aphids per pot was standardized to 100—150 by trimming plants containing excess aphids. The test compounds were formulated by a standard procedure which involved solution in acetone, addition of an emulsifier, and then serial dilution with water. The potted plants (one pot per concentration tested), infested with 100—150 aphids, were placed on a revolving turntable and sprayed with 100—110 milliliters of test compound formulation by use of a spray gun set at 40 psig. air pressure. This application, which lasted 30 seconds, was sufficient to wet the plants to run-off. As a control, 100—110 milliliters of a water acetone emulsifier solution containing no test compound were also sprayed on infested plants. After spraying, the pots were placed on their sides on a sheet of white standard mimeograph paper which had been previously ruled to facilitate counting. Temperature and humidity in the test room during the 24-hour holding period were 65—70°F. and 50—70 per cent, respectively. Aphids which fell onto the paper and were unable to remain standing after being uprighted were considered dead. Aphids remaining on the plants were observed closely for movement and those which were unable to move the length of the body upon stimulation by prodding were considered dead.

After correcting for natural mortality by means of Abbott's formula, the LD_{50} in ppm was estimated by plotting the logarithm of the concentration versus probit of the mortality in the usual manner.

Armyworm Leaf Dip Test

Larvae of the southern armyworm (*Prodenia eridania, Cram*), reared on Tendergreen bean plants at a temperature of 80±5°F. and a relative humidity of 50±5 per cent, constituted the test insects. The test larvae were removed from the colony and held without food for four hours prior to the test. The test compounds were formulated by a standard procedure which involved solution in acetone, addition of an emulsifier, and the serial dilution with water. Paired seed leaves, existed from Tendergreen bean plants, were dipped in the test formulations until thoroughly wetted, excess liquid being removed by gentle shaking. While the leaves were drying in a ventilated hood, wilting was prevented by placing the stems in water. When dry, the paired leaves were separated and each one was placed in a 9-centimeter Petri dish lined with moistened filter paper. Four randomly selected larvae were introduced into each dish and the dishes were closed. The closed dishes were labeled and held at 80—85°F. for three days. Although the larvae could easily consume the whole leaf within twenty-four hours, no more food was added. Larvae which were unable to move the length of the body, even upon stimulation by prodding, were considered dead. After correcting for natural mortality by means of Abbott's formula, the LD_{50} in ppm was estimated by plotting the logarithm of the concentration versus probit of the mortality in the usual manner.

Mexican Bean Beetle Leaf Dip Test

Third instar larvae of the Mexican bean beetle (*Epilachna varivestis*, Muls.), reared on Tendergreen bean plants at a temperature of 80±5°F. and 50±5 per cent relative humidity, were the test insects. The test compounds were formulated by a standard procedure which involved solution in acetone, addition of an emulsifier, and then serial dilution with water. Paired seed leaves excised from Tendergreen bean plants were dipped in the test formulation until thoroughly wetted, excess liquid being removed by gentle shaking. While the leaves were drying under a hood, wilting was prevented by placing the stems in water. When dry, the paired leaves were separated and each was placed in a 9-centimeter Petri dish lined with moistened filter paper. Four randomly selected larvae were introduced into each dish, and the dishes were closed. The closed dishes were labeled and held at a temperature of 80±5°F. for three days. Although the larvae could easily consume the leaf with 24 to 48 hours, no more food was added. Larvae which were unable to move the length of the body, even upon stimulation, were considered dead. After correcting for natural mortality by means of Abbott's formula, the LD_{50} in ppm was estimated by plotting the logarithm of the concentration versus probit of the mortality in the usual manner.

Fly Bait Test

Four to six day old adult house flies (*Musca domestica*, L.), reared according to the specifications of the Chemical Specialties Manufacturing Association (Blue Book, MacNair-Dorland Co., N.Y. 1954: pages 243—244, 261) under controlled conditions of 80±5°F. and 50±5 per cent relative humidity, were the test insects. The flies were immobilized by anesthetizing with carbon dioxide and twenty-five immobilized individuals, males and females, were transferred to a cage con-

sisting of a standard food strainer about five inches in diameter which was inverted over blotting paper. The test compounds were formulated by a standard procedure which involved solution in acetone, addition of an emulsifier and then serial dilution with water. Fifteen milliliters of the test formulation were added to a soufflè cup containing a one-inch square of an absorbent pad. This bait cup was introduced and centered on the blotting paper under the food strainer prior to admitting the flies. The caged flies were allowed to feed on the bait for twenty-four hours, at a temperature of 80±5°F. and the relative humidity of 50±5 per cent. Flies which showed no sign of movement on prodding were considered dead. After correcting for natural mortality by means of Abbott's formula, the LD_{50} in ppm was estimated by plotting the logarithm of the concentration versus probit of the mortality in the usual manner.

Mite Foliage Spray Test

Adults and nymphal stages of the two-spotted mite (*Tetranychus telarius* (L.), reared on Tendergreen bean plants at 80±5°F. and 50±5 per cent relative humidity, were the test organisms. Infested leaves from a stock culture were placed on the primary leaves of two bean plants six to eight inches in height, growing in a two-and-a-half inch clay pot. 150—200 Mites, a sufficient number for testing, transferred from the excised leaves to the fresh plants in a period of twenty-four hours. Following the twenty-four hour transfer period, the excised leaves were removed from the infested plants. The test compounds were formulated by a standard procedure which involved solution in acetone, addition of an emulsifier, and then serial dilution with water. The potted plants (one pot per concentration) were placed on a revolving turntable and sprayed with 100—110 milliliters of test compound formulation by use of a DeVilbiss spray gun set at 40 psig. air pressure. This application, which lasted 30 seconds, was sufficient to wet the plants to run-off. As a control, 100—110 milliliters of a water solution containing acetone and emulsifier in the same concentrations as the test compound formulation, but containing no test compound, were also sprayed on infested plants. The sprayed plants were held at 80±5°F. and 50±5 per cent relative humidity for six days, after which a mortality count of motile forms was made. Microscopic examination for motile forms was made on the leaves of the test plants. Any individual which was capable of locomotion upon prodding was considered living. After correcting for natural mortality by means of Abbott's formula, the LD_{50} in ppm. was estimated by plotting the logarithm of the concentration versus probit of the mortality in the usual manner.

Mite Systemic Test

Adults and nymph stages of the two-spotted mite (*Tetranychus telarius* L.), reared on Tendergreen bean plants at 80±5°F. and 50±5 per cent relative humidity, were the test organisms. Infested leaves from a stock culture were placed on the primary leaves of two bean plants six to eight inches in height, growing in a two-and-a-half inch clay pot. 150—200 Mites, a sufficient number for testing, transferred from the excised leaves to the fresh plants in a period of twenty-four hours. The test compounds were formulated by a standard procedure of solution in acetone, addition of an emulsifier, and then serial dilution with water. The potted plants were placed in 4 oz. paper containers, and thirty milliliters of the test formulation were drenched into the pot containing the infested plants. The treated plants were held for forty-eight hours at 80±5°F. and 50±5 per cent relative humidity. After the forty-eight hour holding period, microscopic examination for motile forms was made on the leaves of the test plants. Any individual capable of locomotion upon prodding was considered living. After correcting for natural mortality by means of Abbott's formula, the LD_{50} in ppm. was estimated by plotting the logarithm of the concentration varsus probit of the mortality in the usual manner.

Nematocide Test

Infective migratory larvae of the root-knot nematode (*Meloidogyne incognita*, var.*acrita*), reared in the greenhouse on roots of Coleous plants constituted the test organism. Infected Coleus plants were removed from the culture and the roots were chopped very finely. A small amount of these choppings was added to a pint Mason jar containing approximately 180 cubic centimeters of soil. The jar was capped and incubated for one week at room temperature. During the incubation period eggs of the nematode hatch and the larval forms migrate into the soil. The test compounds were formulated by a standard procedure of solution in acetone, addition of an emulsifier, and the serial dilution with water. Ten milliliters of the test formulation were added to each of two jars for each dose tested. Thus each jar contained 25 milligrams of test compound, an amount roughly equivalent to 75 pounds per acre. Following the introduction of the test formulation, the jars were capped and the contents thoroughly mixed on a ball mill for five minutes. The jars remained capped at room temperature for 48 hours whereupon the contents were transferred to 3-inch pots. These pots were then seeded with cucumber as an indicator crop and placed in the greenhouse where they were cared for in the usual fashion for approximately three weeks. The cucumber plants were removed from the pots and the soil was wash-

ed from the roots. The amount of galling was determined by visual inspection and rated according to the following designations:

5=no galling; perfect control
4=very light galling
3=light galling
2=moderate galling
1=severe galling, equal to untreated plants

The controls exhibited no pesticidal activity.

The carbamoyloximes contemplated in this invention may be applied as insecticides, acaracides and nematocides according to methods known to those skilled in the art. Pesticidal compositions containing the compounds as the active toxicant will usually comprise a carrier and/or diluent, either liquid or solid.

Suitable liquid diluents and/or carriers include water, petroleum distillates, or other liquid carriers with an without surface active agents. Liquid concentrates may be prepared by dissolving one of these compounds with a non-phytotoxic solvent such as acetone, xylene, or nitrobenzene and dispersing the toxicants in water with the aid of suitable surface active, emulsifying and dispersing agents.

The choice of dispersing and emulsifying agent and the amount employed is dictated by the nature of the composition and the ability of the agent to facilitate the dispersion of the toxicant. Generally, it is desirable to use as little of the agent as is possible, consistent with the desired dispersion of the toxicant in the spray so that rain does not re-emulsify the toxicant after it is applied to the plant and wash it off the plant. Nonionic, anionic, or cationic dispersing and emulsifying agents may be employed, for example, the condensation products of alkylene oxides with phenol and organic acids, alkyl aryl sulfonates, complex ether alcohols and quaternary ammonium compounds.

In the preparation of wettable powder or dust or granulated compositions, the active ingredient is dispersed in and on an appropriately divided solid carrier such as clay, talc, bentonite, diatomaceous earth and fullers each. In the formation of the wettable powders the aforementioned dispersing agents as well as lignosulfonates can be included.

The required amount of the toxicants contemplated herein may be applied per acre treated in from 1 to 200 gallons or more of liquid carrier and/or diluent in from 5 to 500 pounds of inert solid carrier and/or diluent. The concentration in the liquid concentrate will usually vary from 10 to 95 per cent by weight and in the solid formulations from 0.5 to 90 per cent by weight. Satisfactory sprays, dusts, or granules for general use contain from ¼ to 15 pounds of active toxicant per acre.

The pesticides contemplated herein prevent attack by insects, mites, and nematodes upon plants or other material to which the pesticides are applied, and they have high residual toxicity. With respect to plants they have a high margin of safety in that when used in sufficient amount to kill or repel the insects, they do not burn or injure the plant, and they resist weathering which includes wash-off caused by rain, decomposition by ultraviolent light, oxidation, or hydrolysis in the presence of moisture or, at least, such decomposition, oxidation, and hydrolysis as would materially decrease the desirable insecticidal characteristic of the toxicants or impart undesirable characteristics, for instance, phytotoxicity, to the toxicants. The toxicants are so chemically inert that they are compatible with substantially any other constituents of the spray schedule, and they may be used in the soil, upon the seeds, or the roots of plants without injuring either the seeds or roots of plants, yet by inhibition or root uptake they will kill the pests feeding thereon.

It also has been found that the carbamoyloximes of this invention can be synergized with a wide-variety of compounds except acidic and phenolic compounds or compounds readily metabolized thereto. Little or no synergism has been observed with compounds highly active as pesticides by themselves. Compounds showing moderate to poor pesticidal activity yet possessing good anticholinesterase properties are most likely to be synergized. The carbamoyloximes herein can be synergized with synergists such as piperonyl butoxide, methylenedioxyphenyl compounds, and 2-(3,5 - dichloro - 2 - biphenylyloxy)triethylamine. In general, those synergists which are known to synergize the carbamate pesticides also can be used to synergize the carbamoyloximes of this invention such as those synergists disclosed in the U.S. Patents Nos. 2,904,463, 2,904,464, and 2,904,465, incorporated herein by reference.

Table III illustrates synergistic compositions composed of carbamoyloximes of this invention and piperonyl butoxide as synergist and their affect on the house fly.

TABLE III

Carbamoyloxime	LD_{50} to House Flies in ppm Carbamoyloxime	
	Alone	With 1000 ppm P.B.*
2-Cyano-2-Methylcyclopentanone N-Methylcarbamoyloxime	20	1.5
2-Methyl-2-Nitro-3-Butanone N-Methylcarbamoyloxime	44	3.5
2-Methyl-2-Nitrocyclopentanone N-Methylcarbamoyloxime	22	<1.5
2-Methyl-2-Nitrocyclohexanone N-Methylcarbamoyloxime	126	<4.0

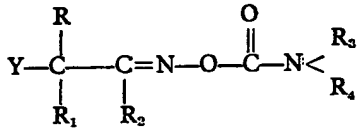
*piperonyl butoxide; non-toxic to house flies at 1000 ppm.

From Table III it can be clearly seen that a synergistic affect is evident from the various compositions of carbamoyloximes and piperonyl butoxide. For example, with 2-cyano-2-methylcyclopentanone N - methylcarbamoyloxime alone, it took 20 ppm of the carbamoyloxime to kill 50 per cent of the house flies whereas 50 per cent of the house flies were killed with only 1.5 ppm of the same carbamoyloxime together with 1000 ppm piperonyl butoxide. As noted in Table III, piperonyl butoxide is not toxic to house flies at 100 ppm. It is believed that the results shown in Table III clearly point out synergism. The procedure employed in Table III is as noted herein with respect to the test procedure for the fly bait test.

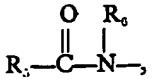
A concentration range, by weight of from 20 parts synergist: 1 part carbamoyloxime to 1 part synergist: 5 parts carbamoyloxime are expected to give a synergistic effect.

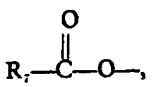
WHAT WE CLAIM IS:—

1. A carbamoyloxime having the general formula:

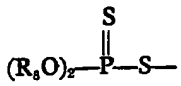
(I) 

wherein Y is a nitro, cyano, thiocyanato,





or



group; R and R_1 are each individually hydrogen or alkyl containing up to 4 alkyl carbon atoms with at least one of R and R_1 being alkyl at all times; R_2, R_3, R_4, R_5, R_6 and R_7 are each individually hydrogen or alkyl containing up to 4 carbon atoms; R_8 is alkyl; R and R_1 or R_1 and R_2 can complete an aliphatic carbocyclic ring containing from 4 to 7 ring carbon atoms; when R and R_1 are both alkyl, one or more of the hydrogen atoms on one only of these two alkyl groups can be substituted; the aliphatic carbocyclic rings completed by $R+R_1$ or R_1+R_2 can be substituted.

2. A carbamoyloxime as claimed in claim 1 in which, when one or more of the R's is alkyl the alkyl is methyl.

3. A carbamoyloxime as claimed in claim 1 or 2 in which both R and R_1 are alkyl and one or more of the hydrogen atoms on one only of the alkyl groups is substituted by cyano, nitro, methoxy, methylthio, halogen, trifluoromethyl, amido or thiocyanato.

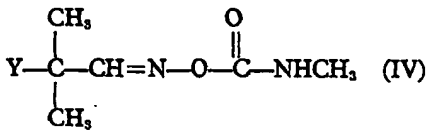
4. A carbamoyloxime as claimed in claim 1 in which $R+R_1$ or R_1+R_2 form part of a carbocyclic ring and said ring is substituted by one or more of the substituents as defined in claim 3, or by alkyl containing up to 4 alkyl carbon atoms.

5. A carbamoyloxime as claimed in claim 1 in which R_2 is hydrogen or methyl, R and/or R_1 is methyl and R_3 and/or R_4 is hydrogen or alkyl of 1 to 4 carbon atoms.

6. A carbamoyloxime as claimed in claim 5 in which the total number of carbon atoms in the R, R_1, R_2, R_3 and R_4 groups does not exceed ten.

7. A carbamoyloxime as claimed in claim 5 or 6 in which both R and R_1 are methyl and R_3 and/or R_4 are hydrogen or methyl.

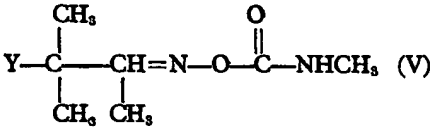
8. A carbamoyloxime as claimed in claim 1 which has the general formula:



(IV)

wherein Y is as defined in claim 1.

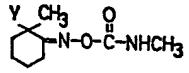
9. A carbamoyloxime as claimed in claim 1 which has the general formula:



(V)

wherein Y is as defined in claim 1.

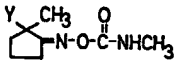
10. A carbamoyloxime as claimed in claim 1 which has the general formula:—



(VI)

wherein Y is as defined in claim 1.

11. A carbamoyloxime as claimed in claim 1 which has the general formula:



wherein Y is as defined in claim 1.

12. 2-Methyl-2 - nitrocyclohexanone N-methylcarbamoyloxime.

13. 2-Methyl - 2 - nitrocyclopentanone N-methylcarbamoyloxime.

14. 2-Methyl - 2 - nitro-3-butanone N-methylcarbamoyloxime.

15. 2-Methyl - 2 - cyanocyclopentanone N-methylcarbamoyloxime.

16. 2-Methyl-(5 or 4)-cyano-2-nitrocyclohexanone N-methylcarbamoyloxime, being the compound described in Example XX.

17. 2-Methyl-2 - nitropropionaldehyde N-methylcarbamoyloxime.

18. 2-Cyano-2-methylpropionaldehyde N-methylcarbamoyloxime.

19. 2-Cyano-2-methyl - 3-butanone N-methylcarbamoyloxime.

20. 2-Cyano-2 - methylcyclohexanone N-methylcarbamoyloxime.

21. 2-Formamido-2-methyl-3-butanone N-methylcarbamoyloxime.

22. 2-Formamido-2 - methylpropionaldehyde N-methylcarbamoyloxime.

23. 2-(N'-methylformamido) - 2 - methylpropionaldehyde N-methylcarbamoyloxime.

24. 2-Formyloxy - 2 - methylpropionaldehyde N-methylcarbamoyloxime.

25. 2-Cyano - 2 - methylbicyclo [2.2.1] heptan-3-one N-methylcarbamoyloxime.

26. 2-Methyl - 2 - nitrobicyclo [2.2.1] heptan-3-one N-methylcarbamoyloxime.

27. 2-Acetamido - 2 - methylpropionaldehyde N-methylcarbamoyloxime.

28. 2-Acetamido-2-methyl-3-butanone N-methylcarbamoyloxime.

29. 2-Methyl - 2-(O,O'-diethylthionophosphonothio)-propionaldehyde N-methylcarbamoyloxime.

30. 2-Methyl-2 - acetoxypropionaldehyde N-methylcarbamoyloxime.

31. 2-Methyl-2 - nitrocycloheptanone N-methylcarbamoyloxime.

32. Methyl-1-nitrocyclopentyl ketone N-methylcarbamoyloxime.

33. 2-Ethyl-2 - nitrocyclopentanone N-methylcarbamoyloxime.

34. 2-Ethyl - 2 - nitrocyclohexanone N-methylcarbamoyloxime.

35. 3-Ethyl-3-nitro-2-pentanone N-methylcarbamoyloxime.

36. 2-Methyl-2 - nitrocyclobutanone N-methylcarbamoyloxime.

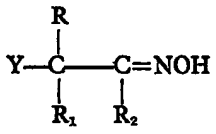
37. 2-Cyano-2,5-dimethylcyclohexanone N-methylcarbamoyloxime.

38. 2-Cyano-5-isopropyl-2 - methylcyclohexanone N-methylcarbamoyloxime.

39. A carbamoyloxime substantially as hereinbefore described with particular reference to any of the foregoing Examples.

40. Pesticidal compositions containing a pesticidally acceptable carrier and, as an active toxicant a carbamoyloxime as claimed in any of claims 1 to 41.

41. A process for the production of a carbamoyloxime of formula IX which comprises reacting an oxime having the general formula



(VIII)

wherein Y, R, R_1 and R_2 are as defined in claim 1, with methyl isocyanate.

42. A process as claimed in claim 41 which is performed in an inert organic solvent.

43. A process as claimed in claim 41 or 42 which is performed in the presence of a tertiary amine or organotin catalyst.

44. A process as claimed in any of claims 41 to 43 which is performed at 10 to 130°C.

45. A process as claimed in claim 44 which is performed at between room temperature and 80°C.

46. A process as claimed in any of claims 41 to 45 which is performed under a pressure of 1 to 10 atmospheres absolute.

47. A process as claimed in claim 46 which

is performed under a pressure of 2 to 3 atmospheres.

48. A process as claimed in any of claims 42 to 47 which is performed in a ketone or acetonitrile as solvent.

49. A process as claimed in any of claims 43 to 48 in which the catalyst is used in an amount of 0.1 to 1.0 weight per cent based on the weight of the oxime and methyl isocyanate.

50. A process as claimed in any of claims 41 to 49 in which the mol ratio of methyl isocyanate to oxime is equimolar or an excess of methyl isocyanate is employed.

51. A process for the production of a carbamoyloxime according to claim 1 which comprises (a) reacting an oxime as defined in claim 41 with phosgene to produce a chloroformate and (b) reacting the chloroformate with ammonia or an amine having the general formula A_3 R_4 NH wherein R_3 and R_4 are as defined in claim 1, in the presence of a solvent for the amine at −40°C to 80°C.

52. A process as claimed in claim 51 in which the chloroformate is reacted with ammonia.

53. A process as claimed in claim 51 in which the amine is methylamine or dimethylamine.

54. A process as claimed in any of claims 51 to 53 in which the reaction with phosgene is performed in the presence of a hydrogen chloride acceptor.

55. A process as claimed in claim 54 in which the acceptor is dimethylaniline.

56. A process as claimed in claim 54 or 55 in which a solution of phosgene in toluene or diethyl ether is added dropwise to a solution of the oxime in toluene or diethyl ether.

57. A process as claimed in any of claims 51 to 56 in which the reaction with phosgene is performed at from −30°C. to 40°C.

58. A process as claimed in claim 57 in which the reaction with phosgene is performed at a temperature between 0°C. and room temperature.

59. A process as claimed in any of claims 51 to 58 in which the solvent is water, dioxane, toluene or chloroform.

60. A process as claimed in any of claims 51 to 59 in which the reaction with ammonia or an amine amine is performed at a temperature below 40°C.

61. A process for the production of a carbamoyloxime substantially as hereinbefore described with particular reference to any of the foregoing Examples.

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12, Church Street, Liverpool, 1,
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.